First Detection of Non-Chlorinated Organic Molecules Indigenous to a Martian Sample

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Introduction: The Sample Analysis at Mars (SAM) instrument onboard Curiosity can perform pyrolysis of martian solid samples, and analyze the volatiles by direct mass spectrometry in evolved gas analysis (EGA) mode, or separate the components in the GCMS mode (coupling the gas chromatograph and the mass spectrometer instruments). In addition, SAM has a wet chemistry laboratory designed for the extraction and identification of complex and refractory organic molecules in the solid samples [1]. The chemical derivatization agent used, *N*-methyl-*N*-*tert*-butyldimethylsilyl-trifluoroacetamide (MTBSTFA – Fig. 1), was sealed inside seven Inconel metal cups present in SAM. Although none of these foil-capped derivatization cups have been punctured on Mars for a full wet chemistry experiment, an MTBSTFA leak was detected and the resultant MTBSTFA vapor inside the instrument has been used for a multi-sol MTBSTFA derivatization (MD) procedure instead of direct exposure to MTBSTFA liquid by dropping a solid sample directly into a punctured wet chemistry cup [2]. Pyr-EGA, Pyr-GCMS and Der-GCMS experiments each led to the detection and identification of a variety of organic molecules in diverse formations of Gale Crater.

SAM solid sample analyses: The analyses of gases released from the Cumberland (CB) and Mojave (MJ) solid samples were conducted by heating the sample portions in a pyrolysis oven to >800 ºC, at a rate of 35 ºC/min under 1 standard cubic centimeters per min He flow and 1) monitoring the evolved gases with a quadrupole mass spectrometer (EGA mode), and 2) trapping a specific temperature range of evolved gases using hydrocarbon traps containing Tenax TA and GR and then heating the traps to send the gases through one of the six gas chromatographic columns before analysis in GCMS. The MD experiment was conducted as a multi-sol experiment as follows: 1) The first step (MD1) consists of a low temperature heating of the sample from ambient to ~125 ºC at a rate of 35 ºC/min under 1 standard cubic centimeters per min He flow during which time volatiles released from the sample were sent to the SAM hydrocarbon trap (silica beads, Tenax TA, and Carbosieve G) set at a temperature of 5 °C. The sample was then heated from 125 ºC to ~ 250 ºC to decompose perchlorates and other oxychlorine compounds in the sample to release O_2, in order to limit the combustion of possible organic molecules and their MTBSTFA derivatives in the second MD step. The cup was then removed from the pyrolysis oven and placed back into the SMS where the sample could re-adsorb and react with MTBSTFA vapor present in the SMS for 48 hours. 2) The second MD step (MD2) utilized a higher temperature heating from ambient to ~900 ºC to perform derivatization of molecules in the sample that evolve at elevated temperatures, with much less O_2 available in the sample for combustion of organics. In the MD2 step, the entire volatile fraction released from the sample during the heating was sent to the hydrocarbon trap for GCMS analysis

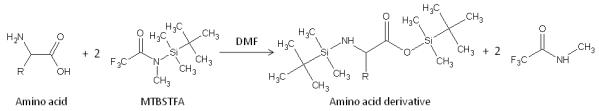

Figure 1: Example MTBSTFA reaction with an amino acid to form the volatile silyl ester derivative and a trifluoro-N-methylacetamide (TFMA) byproduct that are both detectable by the SAM GCMS.

Discussion: SAM permitted the definitive identification of chlorobenzene (C_6H_5Cl - 150-300 part per billion by weight (ppbw)) and C_2 to C_4 dichloroalkanes ($C_2H_4Cl_2$, $C_3H_6Cl_2$ and two isomers of $C_4H_8Cl_2$ - up to 70 ppbw) in GCMS mode, and detection of chlorobenzene in the EGA mode, in multiple portions of the fines from the CB drill hole in the Sheepbed mudstone at Yellowknife Bay (YB) [3]. YB is a lake deposit in the crater floor sediment [4]. These organic molecules were released at relatively low temperature from the CB sample (150-300 ºC). Additional organic molecules indigenous to the CB sample were later discovered in the same set of data, guided by the laboratory breadboards results. These include two isomers of dichlorobenzene and 1,2,3-trichloro-2-methylpropane (Fig. 2).

Although the presence of the chlorohydrocarbons as such in the Sheepbed mudstone cannot be excluded, it is thought that they originate from reactions during SAM pyrolysis between martian chlorine from the perchlorates/oxychlorine, and complex organic aromatic and aliphatic compounds

indigenous to the sample. Therefore, the nature of the chlorohydrocarbon precursor molecules remains unknown. The detection in EGA of unusually high molecular masses released from CB at low temperature, that are consistent with fragments of aromatic hydrocarbons, confirms that more organics are present in the CB mudstone, but are not sufficiently stable and volatile to be identified by GCMS.

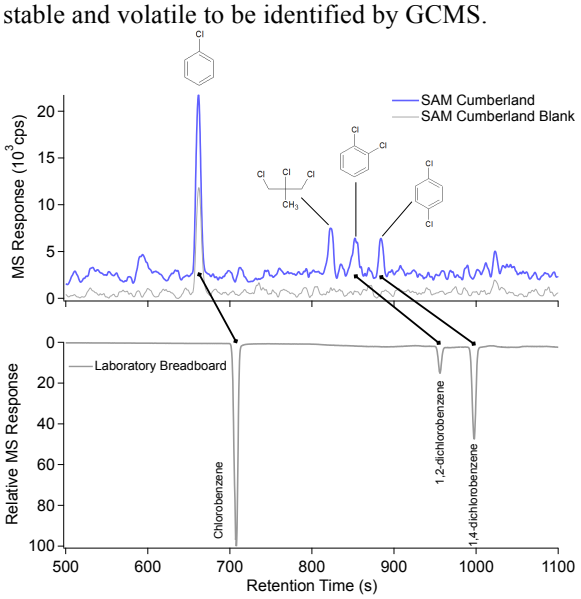

Figure 2: GC identification of organic compounds in SAM CB-5 *vs.* CB-blank-2 (top) and confirmation of their retention time with laboratory run (bottom). SAM chromatogram of Cumberland-5 sample from 500 to 1100 s is reconstructed as such: *m/z* 112 + *m/z* 111*10 + *m/ z* 146*10, smoothed with Box algorithm 31 points. Identification of chlorobenzene (661 s), 1,2,3-trichloro-2-methylpropane (824 s), 1,2-dichlorobenzene (854 s) and 1,4-dichlorobenzene (885 s). The retention times obtained from the laboratory run on GC-5 breadboard in SAM-like conditions were essential to detect and confirm the identification of chlorobenzene and dichlorobenzene isomers.

In Figure 3, several key masses detected by GCMS that correspond to potential high molecular weight MTBSTFA reaction products are plotted. Several masses up to *m/z* 358 (the highest yet detected after pyrolysis of a sample by SAM on Mars) are observed in the MD2 GCMS analysis of the CB triple portion mudstone sample, but were not identified above background level in the twice-heated CB residue analysis that served as a control (*e.g. m/z* 281 at retention time 13.1 min, Fig. 2). Numerous peaks were detected by GCMS above background and we are continuing to work to identify the derivatized compounds by comparison to mass spectral libraries of known MTBSTFA derivatives and by analysis of the fragmentation patterns. Our preliminary results from MD2 compared to the control experiment indicate that in addition to the low temperature chlorinated organics release discussed above, several aromatic hydrocarbons may be present and derivatized in the high temperature portion of the sample. Chlorobenzene was also detected by GCMS in the MD experiments. The presence of all those compounds indicates that enough MTBSTFA was present to perform derivatization in the sample, as well as downstream in the gas processing system.

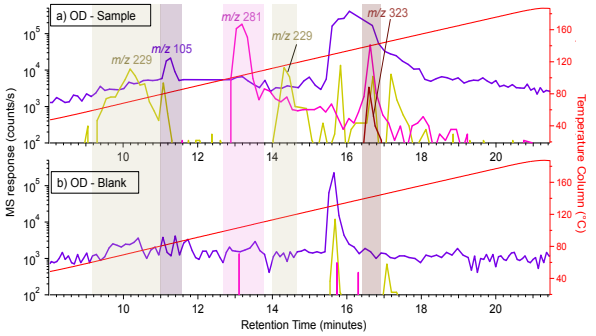

Figure 3: The presence of multiple high mass peaks in the high temperature derivatized CB sample compared to the control suggests a wide range of complex organics in CB.

Additional organic molecules were discovered in the high temperature release of the CB sample. Those molecules all contain the sulphur element and no chlorine indicating that in contrast to the chlorohydrocarbons, these S-containing organics are not reaction products from the combustion of oxychlorine species. The S-containing molecules were also found at a high level in the high temperature release of a subsequent sample, MJ, drilled in the Murray formation at Parhump Hills, at the bottom of the lower mount outcrop at Gale. The compounds were identified in both EGA and GCMS modes [5]. These compounds could be either formed by the high-temperature pyrolysis by combination of S from SO_2 and organics released from the sample, or released as such from CB and MJ.

Conclusion: EGA and GCMS, pyrolysis and derivatization, these techniques are complementary and led to the discovery of multiple organic molecules indigenous to diverse martian solid samples. The MTBSTFA experiment represent the first successful derivatization experiment on Mars. Various state of chlorination of aromatic and aliphatic organics were discovered at low temperature in CB, while S-containing and non-chlorinated derivatized molecules were identified in the high temperature release portion at MJ and CB. As of today, it is undetermined if the origin of those molecules is biotic or abiotic. However, the variety of molecules detected is consistent with the ones found in meteorites such as Murchison or Tissint.

References: [1] Mahaffy, P. R. *et al.* (2012) *Space Sci Rev, 170,* 401-478. [2] Glavin, D. P. *et al.* (2013*) JGR Planets*, Vol. 118, 1–19. [3] Freissinet, C. *et al.* (2015) *JGR Planets.* [4] Grotzinger, J. *et al.* (2015) *Science*. [5] Eigenbrode, J. L. *et al.*, (2015) *AGU conference abstract.*